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31 August 1977

SRI No. PYU-6064

OXIDATION CONTROL IN TNT PRODUCTION

By: Robert L. Simon, Ruben A. Flores, and David S. Ross

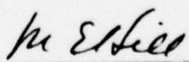
Prepared for:

Commanding Officer
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Picatinny Arsenal, Bldg. 3305
Energetics Process Tech. Branch
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Attention: Dr. Ray Goldstein

Contract No. DAAA21-77-C-0057

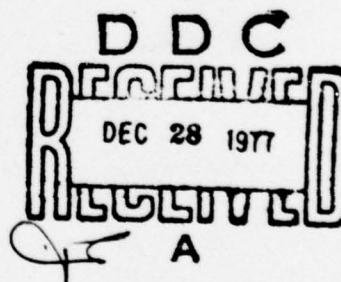
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SUMMARY

This brief study has shown that NO_2 is not the major cause of total oxidation in dinitrotoluene (DNT) nitration media, but that it is linked to side chain oxidation and thus to white compound (WC), an azoxy linked oxidation product of TNT. Nitrogen flushing in anhydrous mixed acids does not lower the total oxidation, but seems to suppress dinitrobenzaldehyde (DNBAl) formation. This procedure could therefore be useful for WC suppression. An increase in reaction temperature had little effect on the oxidation/nitration (Ox/Ni) ratio and on the relative production of aldehyde.


High HNO_3 :DNT ratios favor total oxidation, but an increase in the SO_3 : HNO_3 ratio from 1:1 to 2:1 significantly lowers aldehyde production. Dinitrobenzaldehyde formation is promoted by the presence of 2 phases in the reaction media and by 316 stainless steel, typical of nitrator construction.

In aqueous mixed acids, electrochemical elimination of NO_2 does not reduce oxidation. Free radical inhibitors such as picric acid are not useful in retarding oxidation. The effect of an oxidation promoter for converting side chain intermediates to trinitrobenzoic acid in the DNT nitration media is still unresolved because of experimental problems encountered with the organic salts of Co(III) and Mn(III) .

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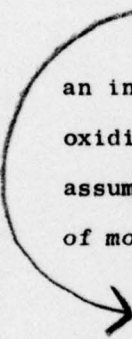
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INTRODUCTION

Large scale production of TNT is complicated by oxidative side reactions that result in undesirable yield losses and by-products. White compound (WC), an azoxy-linked derivative of the oxidation products of TNT, is a solid contaminant in large scale, continuous TNT production. Production must be routinely shut down to remove the WC deposited on surfaces in TNT lines, a process that is costly and time consuming. In addition, a serious explosion in the TNT lines at the Radford Arsenal was found to be indirectly related to WC deposits in the line.

SRI International (formerly Stanford Research Institute) performed an initial study of the oxidation problem.¹ We concluded that the active oxidizer in the higher nitrators was not nitronium ion, as had been assumed, but either NO_2 or NO_3 , both derived from thermal decomposition of molecular nitric acid.

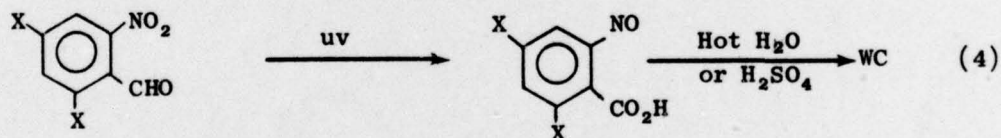
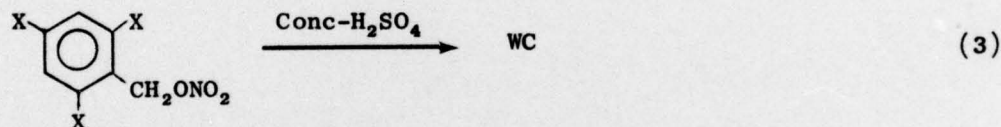
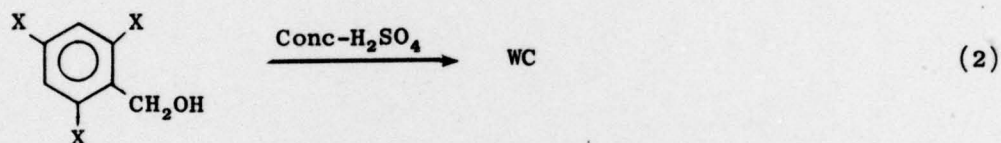
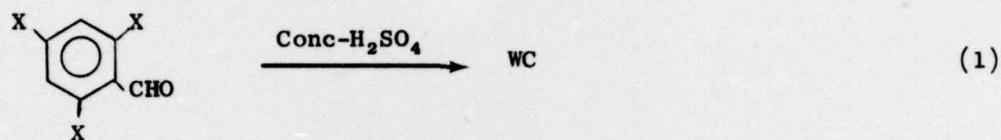


The current program was then begun. The direct aim of this work was to determine if oxidation could be reduced or eliminated by removing the NO_2 that forms during the nitration reaction. We also surveyed the effects of initial SO_3 levels, stainless steel surfaces, and reaction temperature, and the effect of adding oxidation inhibitors and promoters on the oxidation of dinitrotoluene in mixed acid systems.

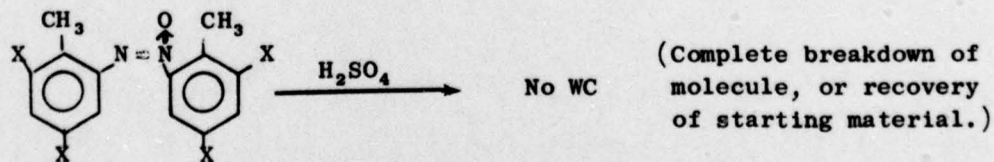


BACKGROUND

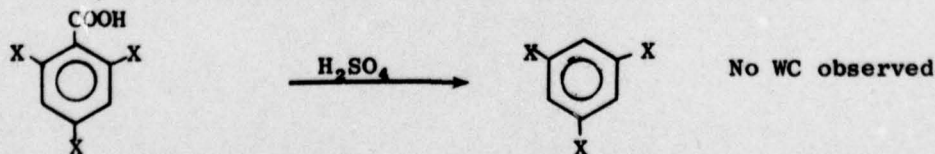
Previous work in acid media²⁻⁴ indicates that WC can be generated by a number of routes ($X = \text{NO}_2$).



Although it has not been examined in detail, the direct reaction of TNT to give WC is unlikely because the coupled dimethyl azoxybenzene gives only decomposition products,³



Also, no evidence exists that trinitrobenzoic acid undergoes coupling.



Therefore, the initial oxidation products of DNT and TNT, di- and trinitrobenzyl alcohol (DNBOH, TNBOH), and di- and trinitrobenzaldehyde (DNBal, TNBal) appear to be the important precursors of WC.

EXPERIMENTAL PROCEDURE

All reactions were run in one of three types of reactors: a 50 ml round bottom flask, a 100 ml round bottom flask with a gas inlet at the bottom, and a two-compartment electrochemical cell.

Two acid mixtures were used in this study. An aqueous system was prepared from a 165.32:14.47 (wt:wt) mixture of 96% H_2SO_4 and 70% HNO_3 . The resulting solution had a H_2SO_4 : HNO_3 mole ratio of 10:1, and was equivalent to a solution of 100% HNO_3 in 94% H_2SO_4 . An anhydrous medium was prepared from 10.20 g 30% oleum and 2.36 g 100% HNO_3 . The resulting solution was equivalent to 9.5 M solution of $\text{NO}_2^+\text{HSO}_4^-$ in 100% sulfuric acid.

Approximately 8.1 mmol of 3,5 DNT (1.47 g) was placed in one of the reactors, and 10 ml of the premixed aqueous acid or 7 ml of the anhydrous acid was added. The mixture was then placed into a 90°C oil bath for 1 hour. The reaction mixtures were protected from the atmosphere by a drying tube, and in some cases, nitrogen was continually flushed through the reactor. At the end of the reaction period, the mixture was quenched on 40 g of ice, extracted with 6 X 35 ml methylene chloride, washed with 6 X 35 ml saturated sodium chloride solution, dried over magnesium sulfate, and vacuum filtered. The organic solvent was removed and the solid product was dried in vacuum at 22°C until it was at constant weight. The product was then dissolved into 100.0 ml ethyl acetate in a volumetric flask, a known amount of hexadecane was added as an internal standard, and the mixture analyzed by gas chromatography (gc).

The gc conditions were:

Column:	OV-17 (10%) on 80/100 gas chromatograph Q
Column temperature:	2 min at 150°C, linear program of 16°C min ⁻¹ to 250°C, 4 min at 250°C
Detector:	Hydrogen flame ionization, 300°C
Carrier gas flow:	60 ml nitrogen min ⁻¹
Hydrogen flow:	60 ml min ⁻¹
Air flow:	240 ml min ⁻¹

The resulting chromatograms clearly showed peaks for the internal standard, unreacted DNT, and the two products 2,3,5-TNT and 3,4,5-TNT. 3,5-DNBal, identified by gas chromatography/mass spectrometry (gc/ms) and virtually the only side product, was observed in substantial quantities in some runs. Figure 1 shows a typical gc scan for a nitration run. Some benzoic acids were determined qualitatively by thin layer chromatography, but were not determined quantitatively.

We have defined total oxidation for any given run as simply the unaccounted for DNT, and include as the quantitative measure of the efficiency of the run, the ratio Ox/Ni. Thus

$$\text{Ox/Ni} = (\Delta\text{DNT} - \Sigma\text{TNT})/\Sigma\text{TNT}$$

where ΔDNT is the consumed DNT, and ΣTNT is the sum of the quantities of the two products 2,3,5-TNT and 3,4,5-TNT.

The total oxidation is the sum of ring oxidation (the formation of phenolic products, which ultimately are destroyed totally to yield CO_x and tetranitromethane), and side chain oxidation (conversion of the methyl group to alcohol, aldehyde, and carboxyl). The latter is of course the ultimate source of WC, and it would be convenient to have some quantitative measure of the degree to which it contributes to the total. The observation of 3,5-DNBal as a major side product offers the opportunity for such a measure, but we could not, because of limited

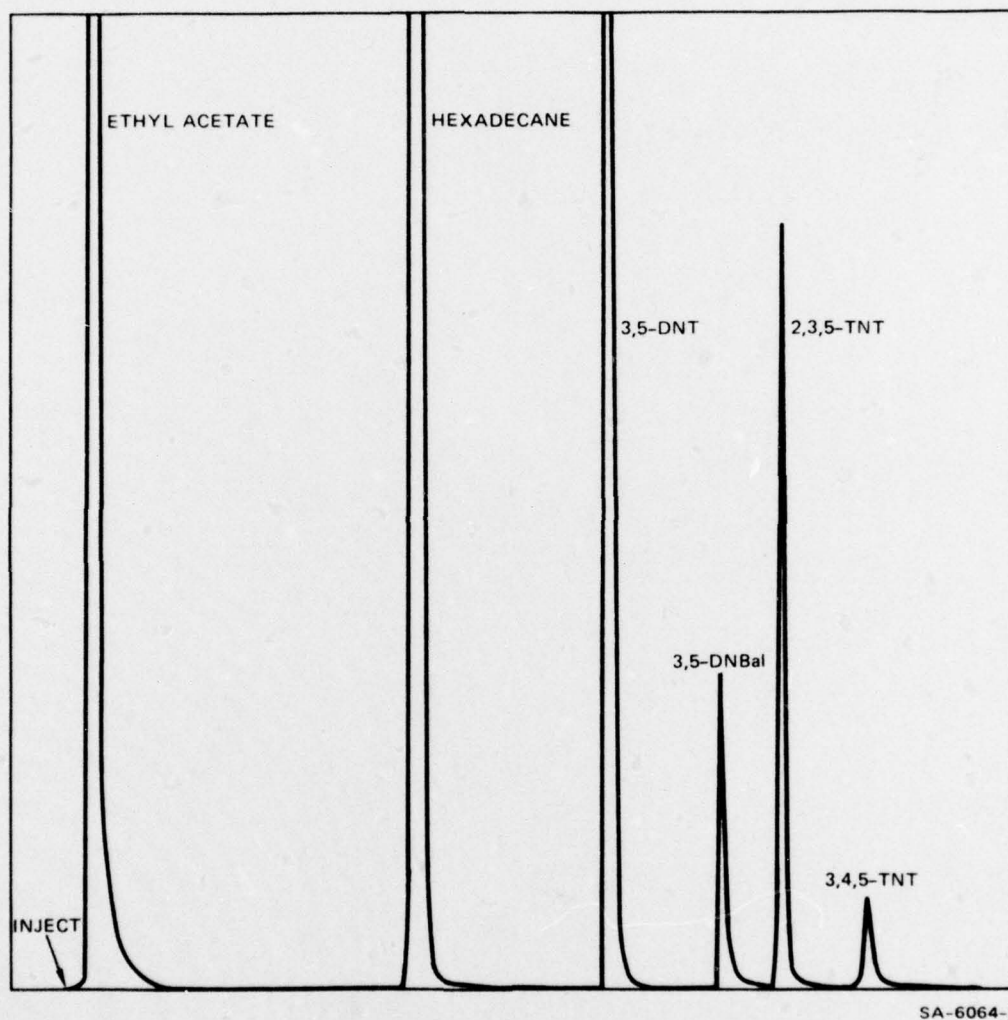


FIGURE 1 TYPICAL GC ANALYSIS TRACE

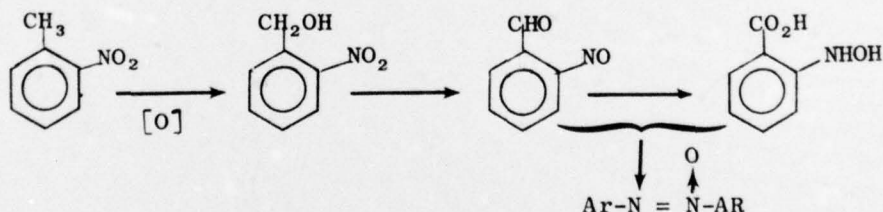
time and funds, synthesize the aldehyde to provide a sample by which to obtain a gc response factor. As a result, no quantitative measure of the contribution side chain oxidation to the total is available. However, we established significant trends in the proportion of side chain oxidation for different reaction conditions by considering the ratio of gc area for 3,5-DNBal and 2,3,5-TNT. These ratios varied significantly and are tabulated along with the other data.*⁵

* For 2,4-DNT nitration, the contribution of side chain oxidation to the total oxidation has been reported to vary with acidity of the medium. In 100% sulfuric acid, side chain oxidation is about 40% of the total. (see Reference 5).

RESULTS AND DISCUSSION

Initially, our efforts were directed toward removing from the nitrating medium those species suspected responsible for the oxidative side reactions evident during TNT production. We began this work with the assumption that the oxidation taking place was due to NO_2 , generated by the thermal decomposition of HNO_3 , and our first approach was to remove NO_2 from the reaction mixture by two different methods, nitrogen ebullition and electrochemical conversion.

We decided to use 3,5-DNT as our sample substrate because it has two major advantages over 2,4-DNT. First, its oxidation/nitration ratio is significantly higher than that for the other DNT isomers, and therefore it serves as a good probe into the oxidation process.¹ Second, its oxidation to alcohol or aldehyde can be conveniently studied without the added complication introduced by *o*-nitro substitution of a subsequent sequence leading to azoxy linkage.



Under our conditions, 3,5-DNT was nitrated to a 5:1 mixture of 2,3,5-TNT and 3,4,5-TNT; 3,5-DNBal was the major side product observed.

The results of all of the work with 3,5-DNT are tabulated in Table 1. The table shows the results of experiments in both aqueous and nonaqueous acid media. The aqueous system was equivalent to about 94% sulfuric acid, with the molar $\text{H}_2\text{SO}_4:\text{HNO}_3$ ratio equal to 10:1. The oleum experiments

Table 1

OXIDATION STUDIES WITH 3,5-DNT AND MIXED ACIDS

Medium ^a	Run No.	Test	Operation	Consumed DNT (%)	TNT Yield (%)		Ox/Ni	3,5-DNEal 2,3,5-TNT
					Δ DNT ^c	$\frac{d}{DNT_0}$		
Aqueous ^a		Blank	To determine handling loss-no HNO ₃ present ^b	-	-	-	-	-
	1	Control	Standard run	19	31	6	2.0	0.34
	2	N ₂ flushing	N ₂ at 1000 ml/min	8	16	1	~ 4.8	^e
	3	N ₂ flushing	N ₂ at 44 ml/min	9	27	3	~ 2.5	^e
	4	Oxidation inhibitor	Picric acid added (3.95 mmol)	8	27	2	~ 2.7	^e
	5	Electro-chemical	Anode + 0.8V	16	27	5	2.5	0.31
	6	Electro-chemical	Anode + 1.8V	17	32	6	2.1	0.41
Nonaqueous ^f	7	Control	Standard run SO ₃ :HNO ₃ :DNT 4.6:4.6:1	62	44	28	1.2	0.41
	8	N ₂ flushing	N ₂ at 500 ml/min	62	46	28	1.2	0.18
	9	N ₂ flushing	N ₂ at 1500 ml/min	60	28	17	2.5	0.17
	10	Temperature	100°C for 1 hr	84	46	39	1.2	0.41
	11	#316 stainless steel	Stainless steel filings (0.4 g)	64	50	33	1.0	1.01
	12	Mole ratio change	SO ₃ :HNO ₃ :DNT 11.4:11.4:1					
	a		9.6: 4.8:1	80	42	33	1.4	0.54
	b		2.3: 2.3:1	28	48	14	1.0	0.21
	c	(2 phases)		39	50	19	1.0	1.39
	13	Ullage	decr. ~ 100	64	35	22	1.8	0.57

^a Mole ratios were H₂SO₄:HNO₃:DNT = 10:1:0.5. Initial quantities were 8.100 mmol DNT (1.47 g) in 10.0 ml reaction medium. Reactions were run at 90°C for 1 hr.

^b H₂SO₄ solution prepared with final quantities of 3,5-DNT and 2,3,5- and 3,4,5-TNT's expected in subsequent runs. Recovered after standard workup: 3,5-DNT, 99.9%, 2,3,5-TNT, 94.4%, 3,4,5-TNT, 83.6%.

^c Yield with respect to consumed DNT.

^d Yield with respect to initial DNT.

^e Conversions too low for adequate measure.

^f Mole ratios unless otherwise stated were SO₃:HNO₃:DNT = 4.6:4.6:1 (used 30% fuming H₂SO₄). Initial quantities were 8.100 mmol DNT (1.47 g) in 6.8 ml reaction medium. Reactions were run at 90°C for 1 hr unless otherwise stated.

were run in systems with $\text{SO}_3:\text{HNO}_3 \geq 1:1$, so that these media can be considered solutions of $\text{NO}_2^+\text{HSO}_4^-$ in sulfuric acid. Appropriate control runs were made for both systems. The $\text{HNO}_3:\text{DNT}$ ratio in the aqueous runs was 2:1. For the oleum runs $\text{HNO}_3:\text{DNT}$ was $\geq 2.3:1$.

In the aqueous system, the Ox/Ni ratios generally fell in the range 2-3. In the nonaqueous system the Ox/Ni ratios were generally in the range 1-2.

Nitrogen Dioxide Removal

N₂ Flushing

We made a total of four flushing runs: Runs 2 and 3 were made in the aqueous system, and runs 8 and 9 in the oleum system. For the aqueous system, the values in the Ox/Ni column show that in the control run (1) under our conditions, the oxidation is about twice the nitration. The Ox/Ni ratio is substantially greater for runs 2 and 3 than for the control run. Additionally, the consumed DNT for these runs is about half that for the control run. Clearly, nitrogen flushing in this system does not reduce total oxidation, and the lower conversions are likely due to nitric acid entrainment by the flowing nitrogen. The low conversions made it impossible to obtain 3,5-DNBal/TNT ratios.

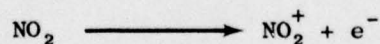
Nitric acid entrainment was in fact subsequently shown to be a major factor in the aqueous system in an experiment in which the mixed acid medium with no DNT present was flushed at 90°C for 1 hr, with the stream directed through a cold trap (-78°C). About 30% of the starting nitric acid was found in the trap at the end of the run. Thus, a substantial fraction of the nitric acid remains un-ionized in the medium.

For the nonaqueous system, the control run (7) showed that, in contrast to the aqueous run, total oxidation is only about 20 to 25% faster than nitration. The result itself is meaningful and will be discussed later. Like the aqueous system, the results for the nonaqueous medium show that little control over total oxidation is derived with N_2 flushing. The consumed DNT for runs 8 and 9 are the same as that for the control run, and consistent with this result is the observation that the trapped N_2 stream for both 8 and 9 showed substantial quantities of NO_2 and tetranitromethane, but no nitric acid.

However, for the nonaqueous system, the 3,5-DNBal/TNT values for runs 8 and 9 suggest that, in contrast to total oxidation, side chain oxidation was substantially reduced by the technique. Comparison of runs 7 and 8, where the DNT consumed and Ox/Ni ratios are the same, shows a reduction in side chain oxidation by better than a factor of two with an N_2 flow rate of 500 ml min^{-1} . This result supports a scheme in which side chain oxidation is due to reaction with NO_2 .

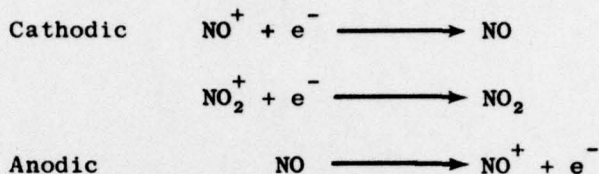
Electrochemical Conversion

Concurrently with the N_2 flushing runs, we studied a second NO_2 elimination technique. We performed nitration runs in an electrolytic cell, hoping to observe the conversion



In our electrochemical approach, we used linear sweep voltametry to determine the potential at which NO_2 is converted to NO_2^+ . The solvent used was the 94% acid nitrating medium to which was added N_2O_4 . We scanned over several potential ranges (0 to +1V, 0 to +1.8V and 0 to +2.0V) at 200 mV sec^{-1} .

In each case, we observed nothing more than oxygen-hydrogen over-voltage. When the nitric acid-sulfuric acid solution of N_2O_4 was diluted about 20-fold with 96% H_2SO_4 we observed the following conversions:



We observed no anodic wave corresponding to the reoxidation of NO_2 ; a similar result was reported by Topol, Osteryoung, and Christie.⁶

Despite this result, we performed two nitrations in an electrolytic cell to see if the oxidation was affected. We chose +0.8V for one of the nitrations because it is the reduction potential obtained in our voltametry sweep for NO_2^+ to NO_2 . The second nitration was run at 1.8V because it is the reported oxidation potential for NO_2 to NO_2^+ in an organic medium (nitromethane).⁷ For both cases, the applied potentials had little effect on both side chain and total oxidation (see Table 1, aqueous runs 5 and 6).

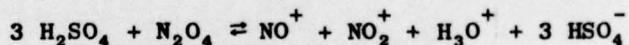
Thus, neither the ebullition nor electrochemical conversion methods for removing NO_2 from the reaction medium had any positive effect on total oxidation. However, ebullition significantly reduced side chain oxidation, suggesting that NO_2 is the side chain oxidizing agent in the system. To test this theory we performed an experiment with a solution of 3,5-DNT in 100% sulfuric acid, through which we passed NO_2 . The solution, consisting of ~ 8.1 moles of 3,5-DNT in 7 ml of 100% H_2SO_4 , was heated to 90°C for 1 hour while about 6 g of NO_2 was slowly bubbled through the acid mixture. Copious NO_2 fumes were present above the reaction mixture.

If NO_2 were the primary oxidant then a significant quantity of DNT should be lost and unaccounted for through ring oxidation at the end of the experiment. On the other hand if NO_2 were only responsible for side chain oxidation, then substantial quantities of 3,5-DNBal would be found.

After the run we recovered 89.6% of the starting DNT, and thus NO_2 does not appear to be responsible for ring oxidation. As discussed below, since water is produced in the dissolution of NO_2 in the acid, the results are properly compared with the aqueous runs, and the 10% conversion is in accord with those results.

While analyses at these low conversions are imprecise, the 3,5-DNBal/2,3,5-TNT ratio was found to be about 0.8, clearly greater than those for the aqueous runs, and larger than most of the entries in Table 1. This result thus supports our suggestion that NO_2 promotes side chain oxidation.

The nitration in the run resulted from the formation of nitronium ion by the known disproportionation of the tetroxide in sulfuric acid media.⁸



Other Studies

Oxidation Inhibition

We next studied other potential oxidation abatement procedures. It has been observed that phenolic materials can act as oxidation inhibitors.⁹ Phenols are already present in small quantities in TNT production systems, but larger quantities could possibly act to suppress or eliminate oxidation. To test this hypothesis, we performed a nitration in the presence of picric acid (run 4).

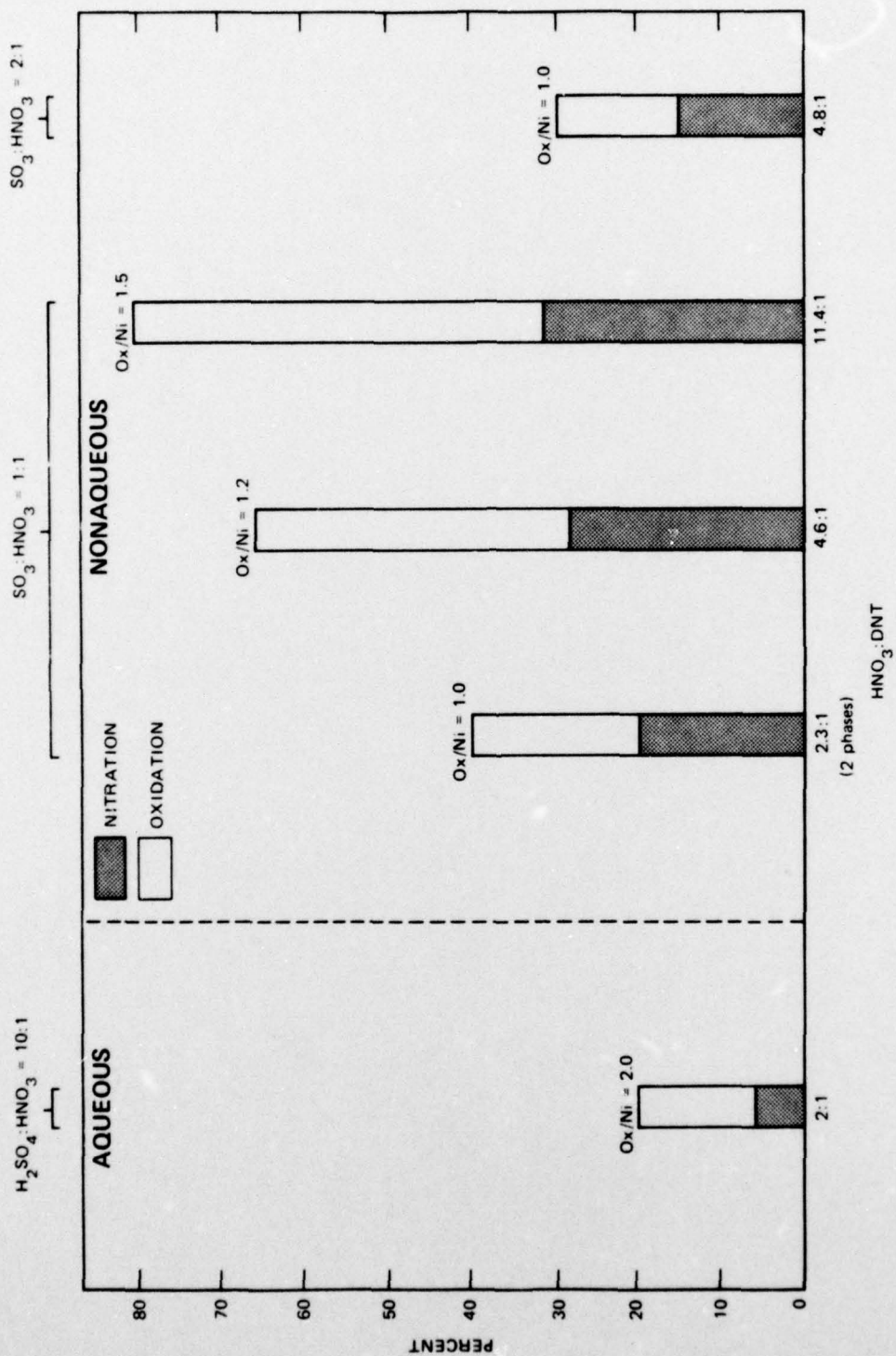
A large quantity of picric acid was used in the reaction, and severe NO_x fuming occurred during the run. As is seen in Table 1 the consumption of DNT was less than half that for the control run (run 1), and the overall TNT production is very small. Relatively large quantities of 3,5-DNBal were observed, and we concluded that this approach was ineffective. No further inhibition work was performed.

Tests of Effects of Temperature, Stainless Steel, Mole Ratios, and Ullage Volume

A number of other experimental variables were tested in several more runs in the anhydrous system, and the results are shown in Table 1, runs 10, 11, 12 and 13. The temperature was increased to 100°C (run 10) with no apparent favorable effect. More DNT was consumed but the fraction of consumed DNT converted to TNT was unchanged. Further, the fraction of oxidized DNT seen as 3,5-DNBal remained about the same. Thus, a 10°C increase in temperature increased both nitration and oxidation by the same factor.

In Run 11, we added 400 mg of 316 stainless steel filings to the standard reaction mixture to assess the effect of the surface of the material from which the large scale nitrators are made. We observed a small decrease in the Ox/Ni ratio. Of interest for this run is the observation of a substantial increase in 3,5-DNBal, and thus in side chain oxidation.

In runs 12a, b, and c, the reactant mole ratios were changed and the results are shown graphically in Figure 2. The bars represent total DNT consumption, broken down into TNT formation and oxidized (unaccounted for) DNT.



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FIGURE 2 COMPILATION OF NITRATION AND OXIDATION DATA FOR REACTIONS OF 3,5-DNT IN NITRATION MEDIA OF 90°C FOR 1 HOUR

As shown in Figure 2, the aqueous system is the least efficient, with an Ox/Ni ratio of 2.0. In anhydrous media the DNT consumptions are greater, with a progression to higher DNT consumption with increasing HNO_3 :DNT ratio. However, the increases in TNT production do not match the increases in consumption, with a resulting increase in the Ox/Ni ratios. Thus, oxidation is more sensitive to HNO_3 concentration than is the nitration, and a low HNO_3 :DNT ratio appears most favorable under these conditions. It would be of interest to investigate systems with even lower ratios.

The 2.3:1 mixture (12c) is a two-phase system. This run, which most closely duplicates TNT line conditions, provided very large quantities of 3,5-DNBal (Table 1) just as seen in the stainless steel run (11). Both runs also showed relatively low Ox/Ni ratios, and these results suggest some oxidation inhibition factor, as of now not understood, that retards not only the substrate oxidation, but also the expected oxidation of 3,5-DNBal to 3,5-DNBA.

Thus, aldehyde accumulates in these systems. Runs 11 and 12c most closely simulate TNT-line conditions, and since DNBal is a WC precursor, we conclude that two phases, as well as the presence of stainless steel, contribute significantly to WC formation.

Finally, comparing the 4.6:1 and 4.8:1 runs with different SO_3 : HNO_3 ratios, (runs 7 and 12b), it can be seen that increasing the quantity of SO_3 substantially reduces the DNT consumption, with a favorable decrease in Ox/Ni ratio. Aldehyde production here is relatively low as well. Thus, at least from these few data, it can be suggested that increased quantities of SO_3 can reduce oxidation, but at the sacrifice of reaction rate.

To test the effect of ullage space (run 13), we decreased the ullage volume by a factor of about 100 by carrying out the reaction in a small flask just large enough to hold the 6 to 7 ml of reaction solution. As shown in Table 1, the consumed DNT value is about the same as that for the control run 7, but the Ox/Ni ratio is substantially greater. Thus oxidation increases, and nitration decreases correspondingly. This result is not easily explained chemically, but ullage volume appears to be an important parameter in TNT production.

Selective Oxidation

Since the reaction TNBOH to form WC is relatively slow, is second order in TNBOH and thus very sensitive to the concentration of the intermediate, some potential advantage might be gained by developing conditions under which the intermediate alcohol is selectively oxidized to relatively inert materials such as trinitrobenzoic acid. With this approach, the alcohol is likely to be significantly more susceptible to oxidation than the parent TNT. It is therefore of interest to seek out conditions where any TNBOH formed is rapidly converted to TNBA before any significant conversion to WC, and with no significant increase in TNT oxidation itself.

We proposed to survey briefly several potential oxidizers for this process, including Co(III) and Mn(III) stearates and acetates. These metals have proven very effective in catalyzing the oxidation of toluene, benzyl alcohol, and benzaldehyde to benzoic acid.¹⁰ We chose 2,4,6-TNBal as the substrate and planned to run a series of reactions using the anhydrous acid system with TNBal, both with and without the metal catalysts. However, we found that the Co(III) and Mn(III) acetates and stearates violently decompose when in the presence of the nitrating medium.

The strong acids react exothermically with the acetate and stearate ligands. The Co(III) and Mn(III) sulfate or nitrate salts could be more suitable for this experiment, however, they are not easily prepared. Therefore this approach was discontinued.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This brief study has shown that NO ₂ is not the major cause of total oxidation in DNT nitration media, but that it is linked to side chain oxidation and thus to WC production. N ₂ flushing in anhydrous, mixed acids does not lower the total oxidation, but seems to suppress DNBal formation. The procedure could therefore be useful for WC suppression. An increase in reaction temperature had little effect on the Ox/Ni ratio and on the relative production of aldehyde. (over please)			

20. High HNO_3 :DNT ratios favor total oxidation, but an increase in the SO_3 : HNO_3 ratio from 1:1 to 2:1 significantly lowers aldehyde production. Aldehyde formation is promoted by the presence of 2 phases and 316 stainless steel.

In aqueous mixed acids, electrochemical elimination of NO_2 does not reduce oxidation. Free radical inhibitors such as picric acid are not useful in retarding oxidation. The effect of an oxidation promoter for converting side chain intermediates to TNBA in the DNT nitration media is still unresolved because of experimental problems encountered with the organic salts of Co(III) and Mn(III) .